

1 **Hydrothermal decomposition of various crystalline celluloses as treated by**  
2 **semi-flow hot-compressed water**

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34 **Abstract**

35 Various types of crystalline celluloses I, II, III<sub>I</sub>, III<sub>II</sub>, IV<sub>I</sub> and IV<sub>II</sub> that have been adjusted for  
36 their degree of polymerization (*DP*) were treated by semi-flow hot-compressed water (HCW)  
37 at 230-270°C/10 MPa/15 min in order to study their chemical decomposition. The treatments  
38 resulted in either partial or complete decomposition of the celluloses and the decomposed  
39 products were primarily recovered as hydrolyzed, dehydrated and fragmented ones as well as  
40 organic acids in the water-soluble (WS) portions. Their results of chemical decomposition  
41 and its kinetics revealed that the celluloses decomposition is dependent on the types of  
42 crystalline celluloses as well as temperature of the HCW treatment. The outcome from the  
43 WS portions at 270°C/10 MPa/15 min showed that the degree of difficulty for decomposition  
44 is lower in group II (cell II, cell III<sub>II</sub>, cell IV<sub>II</sub>) than group I (cell I, cell III<sub>I</sub>, cell IV<sub>I</sub>),  
45 indicating that group II is less resistant to decomposition by HCW treatment. Therefore, the  
46 decomposition behaviors of the cellulose are due to the inherent differences in the crystalline  
47 structures.

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49 **Keywords** Cellulose, Cotton linter, Crystalline structure, Hydrolysis, Semi-flow hot-  
50 compressed water

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## 68 **Introduction**

69           Currently, almost all ethanol from renewable carbon is obtained from food-based  
70 sources such as starch and molasses. The shortage of capacity and competition from food  
71 requirement drives the need for lignocellulose, such as grasses and woods, to serve carbon  
72 resources for promising biofuels [1]. Cellulose as one of the main components in  
73 lignocellulose with approximate production of  $1.5 \times 10^{12}$  tons each year globally has high  
74 potential to be exploited for this purpose [2, 3]. It can be chemically converted into  
75 fermentable saccharides, however, this is usually hindered by its great resistance to  
76 hydrolysis [4].

77           Cellulose is a linear crystalline homopolymer consisting of  $\beta$ -1,4-linked D-  
78 glucopyranose units. It exists in six known polymorphs of celluloses (I, II, III<sub>I</sub>, III<sub>II</sub>, IV<sub>I</sub>, IV<sub>II</sub>)  
79 identified by their characteristic X-ray diffraction (XRD) patterns as well as <sup>13</sup>C nuclear  
80 magnetic resonance (NMR) spectra. In nature, cellulose has high degree of polymerization  
81 (*DP*), in a range of about 6000 to 15000 glucopyranose units [5] which makes it highly  
82 crystalline and not easy to be separated or dissolved in almost any solvents [6,7]. Thus,  
83 numerous biological, chemical, and/or physical treatments such as enzymatic saccharification,  
84 acid/alkali treatments, steam explosion, supercritical and subcritical treatments have been  
85 applied and developed for cellulose hydrolysis [8-14].

86           Hydrothermal treatment in hot-compressed water (HCW) has been proposed as a  
87 promising method to hydrolyze cellulose mostly due to its non-toxic, non-catalytic and  
88 environmentally benign properties [15-18]. Furthermore, over conventional method, it has  
89 advantages such as limited corrosion problem, no sludge generation, low capital and  
90 operational cost, as well as no significant degradation of cellulose at normal operating  
91 conditions [19]. The conventional methods such as acid/alkali treatment and acid/alkali  
92 pretreatment followed by enzymatic hydrolysis are associated with serious economic and  
93 environmental constraints due to the heavy use of chemicals.

94           Hot-compressed water is highly pressurized, high temperature liquid water at  
95 subcritical condition, below the critical point of water at 374°C/22.1 MPa [20]. It is  
96 characterized by a higher ionic product and thus higher concentration of H<sup>+</sup> and OH<sup>-</sup> ions,  
97 compared to ambient water, offering a highly interesting reaction medium for hydrolysis  
98 processes. In addition, acid neutralization is not required because the concentration of H<sup>+</sup> ion  
99 is a function of temperature, and decreases when the temperature is lowered. Many studies  
100 have confirmed that cellulose can be largely hydrolyzed in subcritical water without addition  
101 of a catalyst [21-26].

102 The experimental results using a flow-type HCW treatment showed that glucose yield  
103 increases with increasing temperature [27]. It has less significant degradation reactions as  
104 compared with batch-type treatment that makes it preferable for hydrolysis process of  
105 lignocellulose [28-30]. It has been reported that 4-22 % of cellulose could be hydrolyzed by  
106 flow-type HCW treatment (200-230°C/34.5 MPa/15 min) [31].

107 To the best of authors' knowledge, studies have been done on analysis of cellulose  
108 hydrolysis by using HCW treatment; however, the comprehensive investigation has been  
109 rarely conducted on various crystalline celluloses as feedstocks. The physical characteristics  
110 such as crystallinity and *DP* of various crystalline cellulose residues as treated by semi-flow  
111 HCW were thoroughly explored in previous study together with a brief evaluation on the  
112 water-soluble (WS) portions [32]. Therefore, as a further approach, the primary objective of  
113 this work is to study quantitatively the chemical decomposition from various crystalline  
114 celluloses as treated by semi-flow HCW through the yields of WS portions.

115

## 116 **Materials and Methods**

117 Preparation of various types of crystalline cellulose samples

118 Cotton linter (Buckeye 1AY-500), in the form of cellulose I (cell I), was used to  
119 prepare various types of crystalline celluloses. Cellulose II (cell II) was prepared from cell I  
120 through mercerization by soaking it into 20.0 % of aqueous NaOH solution for 24 h at  
121 ambient condition of temperature (20°C) and pressure (0.1 MPa), followed by washing  
122 thoroughly with water and freeze-drying [33]. As for celluloses III<sub>I</sub> (cell III<sub>I</sub>) and III<sub>II</sub> (cell  
123 III<sub>II</sub>), they were prepared from cell I and cell II, respectively. Cell I and cell II were soaked in  
124 100 % ethylenediamine for 24 h at ambient condition, washed with dried methanol and kept  
125 under vacuum.

126 The prepared cell III<sub>I</sub> and cell III<sub>II</sub> were further used for the preparation of celluloses  
127 IV<sub>I</sub> (cell IV<sub>I</sub>) and IV<sub>II</sub> (cell IV<sub>II</sub>), by firstly soaking them in glycerol for 3 d at ambient  
128 condition. They were then heated in a reaction vessel at 260°C/0.6 MPa for 30 min and  
129 cooled down to ambient condition [34]. The product was, then, washed with water and  
130 acetone successively, and dried in vacuum. Basically, the converted celluloses consisted of  
131 group I (cell I, cell III<sub>I</sub>, cell IV<sub>I</sub>) and group II (cell II, cell III<sub>II</sub>, cell IV<sub>II</sub>). Their chemical  
132 compositions were also analyzed and all these celluloses were found to contain similar  
133 monosaccharide components of about 99.9 wt% glucose and 0.1 wt% xylose [35].

134 To compare the decomposition products from the water-soluble (WS) portions on  
135 various types of crystalline celluloses by semi-flow HCW treatment, cellulose with similar

136 *DP* are necessary for their evaluation. Consequently, these celluloses were adjusted by trial  
137 and error for their *DP*s by changing the treatment condition mentioned above for converting  
138 cell I to various forms of celluloses.

139

140 The determination of *DP* and crystallinity of the celluloses

141 The celluloses were dissolved in 0.5 M cupriethylenediamine (Cuen) by viscometry as  
142 per TAPPI method [36]. The *DP* of the celluloses was then calculated from the intrinsic  
143 viscosity  $[\eta]$  according to the equation  $DP^{0.905} = 0.75[\eta]$  [37]. For the crystallinity  
144 determination, Gaussian functions were used to deconvolute the XRD patterns of various  
145 crystalline celluloses [38]. These XRD patterns were recorded by X-ray diffractometer  
146 Rigaku RINT 2200 [32].

147

148 Treatment of various crystalline cellulose samples by semi-flow HCW treatment

149 The prepared celluloses as starting materials were then treated individually in a semi-  
150 flow HCW system. The conversion system and its operational procedures as explained  
151 elsewhere were adapted for this study [24-26]. Briefly, about 0.4 g of cellulose was treated  
152 individually within a 5 mL reaction vessel. The ambient distilled water from a water tank was  
153 flown through the reaction vessel by a pump in order to pressurize the system at 10 MPa  
154 controlled by a back-pressure regulator. To raise the temperature, the preheating unit  
155 monitored by thermocouples was used to reach at the designated temperatures of 230, 250  
156 and 270°C for about 20 min under 10 MPa and remain constant for additional 15 min, totally  
157 35 min. In addition, another heating unit was installed at the reaction vessel to maintain the  
158 designated temperature in the reaction vessel, into which the HCW was passed through at the  
159 flow-rate of 10 mL/min.

160 These treatments yielded insoluble residues [32] and WS portions. After the HCW  
161 passing through the reaction vessel, the WS portions were cooled down immediately by the  
162 cooling system to terminate all reactions and collected every 5 min. They were allowed to  
163 settle in ambient temperature and pressure for a minimum of 12 h. Though no precipitation  
164 was observed after at least 12 h, it was filtered by 0.45  $\mu\text{m}$  membrane prior to the subsequent  
165 analyses.

166

167 Analytical methods

168 The WS portions collected were analyzed and characterized by using high-  
169 performance anion exchange chromatography (HPAEC), high-performance liquid

170 chromatography (HPLC) and capillary electrophoresis (CE). The HPAEC system (Dionex  
171 ICS-1000 system) equipped with the CarboPac PA-1 column (4 mm x 250 mm) and  
172 electrochemical detector for pulsed amperometric detection was employed and operated at  
173 35°C and flow-rate of 1.0 mL/min under the helium atmosphere for monosaccharides and  
174 cello-oligosaccharides in the WS portions. The mobile phase was a gradient-programmed  
175 mixture of deionized water, 0.2 M NaOH and 2.0 M CH<sub>3</sub>COONa, as eluents. All eluents  
176 contained in 3 separate reservoirs were degassed by an aspirator and subsequently purged  
177 with helium to prevent the absorption of CO<sub>2</sub>.

178 The HPLC system (Shidmadzu, LC-10A) equipped with a Shodex Sugar KS-  
179 801/Ultron PS-80P columns and refractive index/UV-Vis detector was applied. The eluent  
180 used was deionized water at a flow-rate of 1.0 mL/min and oven temperature was set to be  
181 80°C for the columns. The CE (Agilent; Germany) was used to assay the low molecular  
182 weight organic acids. A fused-silica capillary (Agilent; 75 µm diameter, 104 cm total length,  
183 95.5 cm effective length) was used at 15°C.

184 Concentrations of the products in the WS portions were calculated based on the peak  
185 areas on chromatograms obtained from HPAEC, HPLC and CE. A set of standards with  
186 known concentrations, containing the compounds that were to be identified both  
187 quantitatively and qualitatively, was prepared and analyzed together with the samples by  
188 using the relevant analytical equipment as mentioned above [18, 24, 25].

189

## 190 **Results and Discussion**

191 To investigate the decomposition behaviors on various types of crystalline celluloses  
192 by semi-flow HCW treatment, the celluloses must have the same *D*P<sub>s</sub> as the starting  
193 materials. Thus, a direct comparison between the celluloses is feasible, as listed in Table 1.  
194 Treatments by semi-flow HCW were then carried out for these celluloses at temperatures of  
195 230, 250 and 270°C under 10 MPa for 15 min (230-270°C/10 MPa/15 min).

196

### 197 **Decomposition kinetics**

198 The semi-flow HCW treatment decomposed various crystalline celluloses either  
199 partially or completely to the WS portions. The yield on WS portions from various crystalline  
200 celluloses as shown in Fig. 1, is a function of treatment temperatures. At constant treatment  
201 time, the yield on WS portions increased as the temperature increased. They were measurable  
202 even at lower temperature, 230°C/10 MPa, with approximately 10-30 wt% and increased to  
203 more than 70 wt% at higher temperature, 270°C/10 MPa. At 270°C/10 MPa/15 min, cell II

204 was shown to be totally decomposed to WS portions as compared with other celluloses. The  
205 overall results from Fig.1 illustrated that higher yields were obtainable for group II celluloses  
206 than group I.

207 Figure 2 shows the Arrhenius plot of the present results according to the pseudo-first-  
208 order reaction kinetics. The relationship between natural logarithms of reaction constants,  $\ln k$ ,  
209 and  $T^{-1}$  shows good linear fits with the results indicating that the decomposition follows the  
210 pseudo-first-order reaction kinetics. Every parameter used such as time, pressure and  $DP$  on  
211 the celluloses were kept constant, satisfying the assumption that the Arrhenius-plot is  
212 temperature dependent. Though, the data points obtained in this study are only based on three  
213 different temperatures profile, the degree of decomposition could be determined reliably and  
214 the comparison of kinetics on various crystalline celluloses can be done directly.

215 The apparent activation energies,  $E_a$ , for the celluloses can be calculated from Fig. 2.  
216 Activation energy of any reaction mainly explains its degree of temperature-sensitiveness;  
217 reactions with higher  $E_a$  are high in temperature-sensitiveness, while the reactions with lower  
218  $E_a$  are low temperature-sensitive [39]. It can also be said that  $E_a$  is defined as the minimum  
219 energy required for decomposition to occur. The smaller  $E_a$  for decomposition of cellulose  
220 signifies the requirement of less energy for its decomposition and *vice versa*. In Fig.2, it was  
221 shown that different slopes obtained for each of the celluloses suggested different  $E_a$  for  
222 cellulose decomposition in the studied temperature range.

223 Table 2 shows the obtained  $E_a$  for all celluloses within the treatment temperatures.  
224 The  $E_a$  for group I and group II celluloses are, respectively, greater than 70 kJ/mol and in  
225 between 50-60 kJ/mol. It is apparent that the celluloses in group I have higher  $E_a$  than those in  
226 group II, which implies an easier decomposition process for group II celluloses by semi-flow  
227 HCW treatment. However, due to the aforementioned limitations such as limited numbers of  
228 experiments carried out in a relatively narrow temperature range, the obtained  $E_a$  must be  
229 judged critically. The acquired  $E_a$  was based on the best fit curves. As a result, a higher  $E_a$   
230 was obtained for cell IV<sub>I</sub> as compared with cell I and cell III<sub>I</sub>. Since comparison of  $E_a$  was  
231 done between group I and group II, the above observation of group I having higher  $E_a$  than  
232 group II is valid.

233 These  $E_a$  are lower than previously reported, 164 kJ/mol [7] and 145 kJ/mol [40]  
234 without catalysts, whereas, 144 kJ/mol and 100 kJ/mol [41] in dilute sulfuric acid catalyst.  
235 The differences in  $E_a$  could be due to various definitions of decomposition processes and  
236 treatment conditions used. For instance, Sasaki et al. [40] studied just the kinetics of cellulose

237 hydrolysis only at elevated temperatures (above 290°C/25 MPa), whereby in this work the  
238 kinetics of various cellulose decomposition was measured at 230-270°C/10 MPa.

239 Here, the observed decomposition of cellulose in subcritical water appears to be as  
240 good as that occurring in dilute sulphuric acid hydrolysis [41]. Cellulose firstly undergoes a  
241 rapid weight loss and followed by a slow hydrolysis step of the remaining cellulose. The high  
242 reactivity is associated with accessible amorphous regions in cellulose that are more  
243 vulnerable to chemical attacks than the crystalline regions [42]. The reaction temperature has  
244 influence on the solvent properties of water [15, 43]. It has been suggested that the shift in  
245 solvent properties affects the kinetics of cellulose decomposition [44, 45]. However, in this  
246 present work, the constant  $E_a$  implies that the reaction mechanism of the hydrothermal  
247 decomposition is not distinctly affected. The lower  $E_a$  obtained indirectly showed that the  
248 decomposition of various celluloses in this system is a catalytic process, in agreement with  
249 the literature [41].

250

251 Quantification of water-soluble (WS) portions

252 Figure 3 shows the reaction scheme of cellulose I decomposition into hydrolyzed and  
253 degraded products as treated by semi-flow HCW treatment, adapted from [32]. In the present  
254 work, the WS portions for various crystalline celluloses obtained from each treatment were  
255 found to follow a similar decomposition pathway as in Fig. 3. It is important to know the  
256 decomposition pathway of cellulose as the degraded products inhibit the fermentation process  
257 for ethanol production [46].

258 Under the HCW conditions, the ionization constant of water increases with  
259 temperature and the amount of dissociation also increases, compared with normal  
260 temperature and pressure. The glucosidic linkages of cellulose are cleaved and cellulose  
261 starts to hydrolyze into cello-oligosaccharides, and subsequently, hydrolyzed to  
262 monosaccharide of glucose [20, 25, 47, 48]. Isomerization of glucose occurred producing  
263 fructose and mannose. These monosaccharides are unstable at high temperature and thus  
264 some parts of them are further converted into their degraded products such as furfural,  
265 5-hydroxymethyl furfural (5HMF), levoglucosan through dehydration, and erythrose,  
266 glycolaldehyde, methylglyoxal through fragmentation [49]. Prolonged treatment, however,  
267 allows further degradation to take place, generating other products such as organic acids.

268 The resulted WS portion percentages based on the dried weight of cellulose samples  
269 clearly indicated that the celluloses have been converted to the hydrolyzed and degraded  
270 products. The hydrolyzed products are comprised of cello-oligosaccharides, glucose, fructose



271 and mannose, whereas the degraded products consist of dehydrated and fragmented products,  
272 as well as organic acids. Their productions were recorded higher in hydrolyzed products as  
273 compared with degraded products, and more yields were obtained as treatment temperatures  
274 increased.

275 These WS portions were calculated similarly as in the previous studies [24, 25]. The  
276 cello-oligosaccharides were consisted of cellobiose, cellotriose, cellotetraose, cellopentaose,  
277 cellohexaose and other cello-oligosaccharides with the higher *DP*. The more existence of the  
278 cello-oligosaccharides with the higher *DP* shows that the cellulose has more resistance  
279 against hydrolysis by semi-flow HCW treatment. In addition to cello-oligosaccharides and  
280 glucose, a smaller amount of fructose was also detected and only traces of mannose were  
281 identified.

282 A much lower yield of the WS portions obtained at 230°C/10 MPa/15 min (data not  
283 shown) was due to the difficulty of the crystalline structures of celluloses to be hydrolyzed at  
284 such lower temperature [26]. The cello-oligosaccharides observed could be obtained from the  
285 paracrystalline cellulose. The observed fructose is not a sugar component in cotton linter, but  
286 it may be isomerized from glucose after hydrolysis from cellulose [50, 51].

287 To evaluate the decomposition behavior of various crystalline celluloses in details, the  
288 results from 270°C/10 MPa/15 min would be more appropriate, as at this condition,  
289 crystalline cellulose is known to decompose [20, 25, 26]. Table 3 shows the comparison  
290 between hydrolyzed and degraded products for the two groups of cellulose samples at  
291 270°C/10 MPa/15 min. It can be seen that for both group I and group II celluloses, more than  
292 50 wt% of hydrolyzed products were obtained as compared with degraded products. It was  
293 reported that about 31.2, 28.1 and 20.5 wt% of hydrolyzed products obtained from the  
294 cellulose of Japanese cedar, Japanese beech and Nipa frond, respectively [52]. However,  
295 there were no results for *DP* of the cellulose from this study that it can be compared with.  
296 The higher yield in WS portions observed in this present work could probably due to the  
297 shorter *DP* celluloses used for the starting materials.

298 According to Fig. 3, the hydrolyzed products were produced at the early stage of  
299 cellulose decomposition pathway. This could signify that these celluloses have resistance  
300 against decomposition. The total hydrolyzed products for cell I and cell III<sub>I</sub> is similar but  
301 much lesser than cell IV<sub>I</sub>, whereas the highest hydrolyzed products obtained in group II is  
302 from cell III<sub>II</sub>, followed by cell IV<sub>II</sub> and cell II. Overall, celluloses in group II have resulted  
303 more hydrolyzed products than those in group I. The observation is similar for the degraded  
304 products.

305            Figures 4 and 5, respectively, illustrated how the hydrolyzed and degraded products  
306 were obtained at every 5 min intervals at 270°C/10 MPa/15 min. In Fig. 4, only the yields of  
307 cello-oligosaccharides, glucose and fructose were shown. These yields are comparable with  
308 the results in the literatures [20, 24-26]. Based on these results, the cellulose has been cleaved  
309 into cello-oligosaccharides at the early stage of the treatment time and the production of  
310 glucose and fructose was seen to occur simultaneously. Celluloses in both group I and group  
311 II have similar behaviors; however, more products were seen from group II celluloses. The  
312 cello-oligosaccharides and glucose were recovered from the treatment time of 35 min. The  
313 crystalline structure of cellulose remained unchanged at temperatures around 230°C [53], thus,  
314 the WS portions emerged from the time-up (0-20 min treatment time) could be from  
315 paracrystalline cellulose, and the time-at (20-35 min treatment time) was from cellulose.

316            Generally, these monosaccharides are further degraded by dehydration or  
317 fragmentation process [15, 24, 54, 55]. Figure 5 illustrated more dehydrated products were  
318 obtained than fragmented products and organic acids. During the treatments, it can be seen  
319 that the degraded products were generated at almost similar time as the hydrolyzed products  
320 (Fig.4). Moreover, the productions of dehydrated and fragmented products as well as organic  
321 acids were generated concurrently. Both group I and group II celluloses in Fig.5 have the  
322 same trends as in Fig. 4, i.e., more products resulted from group II celluloses. The generation  
323 of hydrolyzed products started to be noticeable from around 3 min (Fig. 4) and followed by  
324 degraded products (Fig. 5) about 10 min later. This sequence is parallel with that shown in  
325 Fig. 3 at which the hydrolyzed products were produced earlier in the decomposition pathway,  
326 and later on followed by the production of degraded products.

327            Figure 6 shows the yield in wt% for the individual degraded products in the WS  
328 portions for both group I and group II celluloses as treated by semi-flow HCW at  
329 270°C/10 MPa/15 min. The dehydrated products detected were consisted of furfural, 5HMF  
330 and levoglucosan, whereas fragmented products such as erythrose, glycolaldehyde and  
331 methylglyoxal. While for organic acids, acetic, formic, lactic and glycolic acids were  
332 identified. The furfural in Fig. 6 can not only be produced from pentose but also from hexose  
333 such as glucose. This means that the formation of furfural is possible without pentose via  
334 five-carbon ketoses pathway as proposed in the literature [56].

335            Glycolaldehyde and erythrose were formed via retro-aldol condensation in  
336 glycolaldehyde/erythrose pathway [44, 51], while methylglyoxal was produced via  
337 glyceraldehyde/dihydroxyacetone pathway in hexose fragmentation. Nevertheless, the  
338 production of methylglyoxal in this case was too minute that it was excluded from Fig.6. The

339 production of furfural and 5HMF was significant as compared with other degraded products.  
340 The organic acids produced are the results of further degradation of dehydrated and  
341 fragmented products [51, 57]. Lactic acid production was only a trace to be included in Fig. 6.  
342 All the sequences of degradation reactions and productions are agreeable with Fig. 3.

343         Based on those results above, it can be seen that group II celluloses dominated both  
344 the hydrolyzed and degraded products as compared with group I celluloses. The result on the  
345 WS portions at 270°C/10 MPa/15 min revealed that the degree of difficulty for  
346 decomposition is greater for celluloses in group I than those in group II.

347

### 348 **Conclusion**

349         This study reveals the essential effects of various crystalline celluloses on their  
350 chemical decomposition and its kinetic behaviors as treated by semi-flow HCW. Both  
351 decomposition rate and  $E_a$  are helpful in defining the degree of difficulty for decomposition  
352 of various crystalline celluloses, however, the  $E_a$  obtained were merely based on empirical  
353 relationships of Arrhenius equation. Consequently, the direct method is more preferable than  
354 the latter. Nevertheless, this study showed the new kinetic data as there was no previous data  
355 on these specific reaction systems.

356         These treatments can be used as viable decomposition media for celluloses at which  
357 under the given treatment conditions, cellulose is more readily hydrolyzed with less degraded  
358 products. Group I celluloses (cell I, cell III<sub>I</sub>, cell IV<sub>I</sub>) have shown to have more resistance to  
359 decompose than group II celluloses (cell II, cell III<sub>II</sub>, cell IV<sub>II</sub>). Based on this evidence, it was  
360 clear that the decomposition behaviors are due to the different crystalline forms of celluloses.  
361 Therefore, it is recommended to transform cellulose I to the other for a better hydrolysis  
362 reaction. These presented data are useful for understanding how various types of crystalline  
363 celluloses are chemically decomposed, providing useful insights to efficient utilization of  
364 lignocellulose for biofuels and biochemicals.

365

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540 **List of figure captions**

541

542 **Fig. 1** The yield on WS portions from various types of crystalline celluloses as treated at  
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545

546 **Fig. 2** The Arrhenius plot for various crystalline celluloses using pseudo-first order reaction  
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555 **Fig. 5** The degraded products of dehydrated, fragmented and organic acids products in the  
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559 **Fig. 6** The degraded products in WS portions from various types of crystalline celluloses as  
560 treated by semi-flow HCW at 270°C/10 MPa/15 min

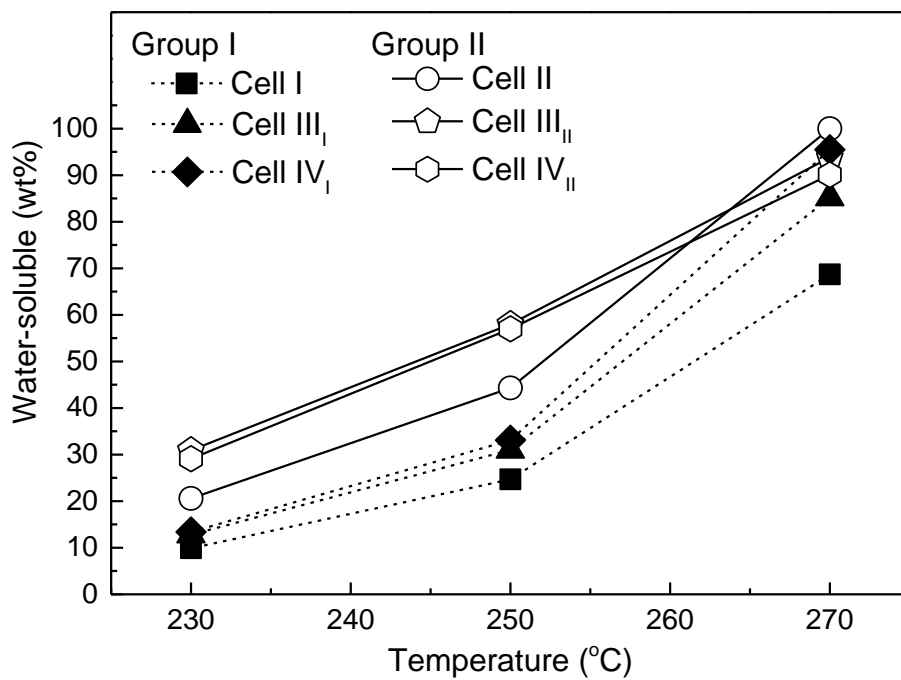


Fig. 1 The yield on WS portions from various types of crystalline celluloses as treated at different temperatures under 10 MPa for 15 min (230-270°C/10 MPa/15 min) by semi-flow HCW

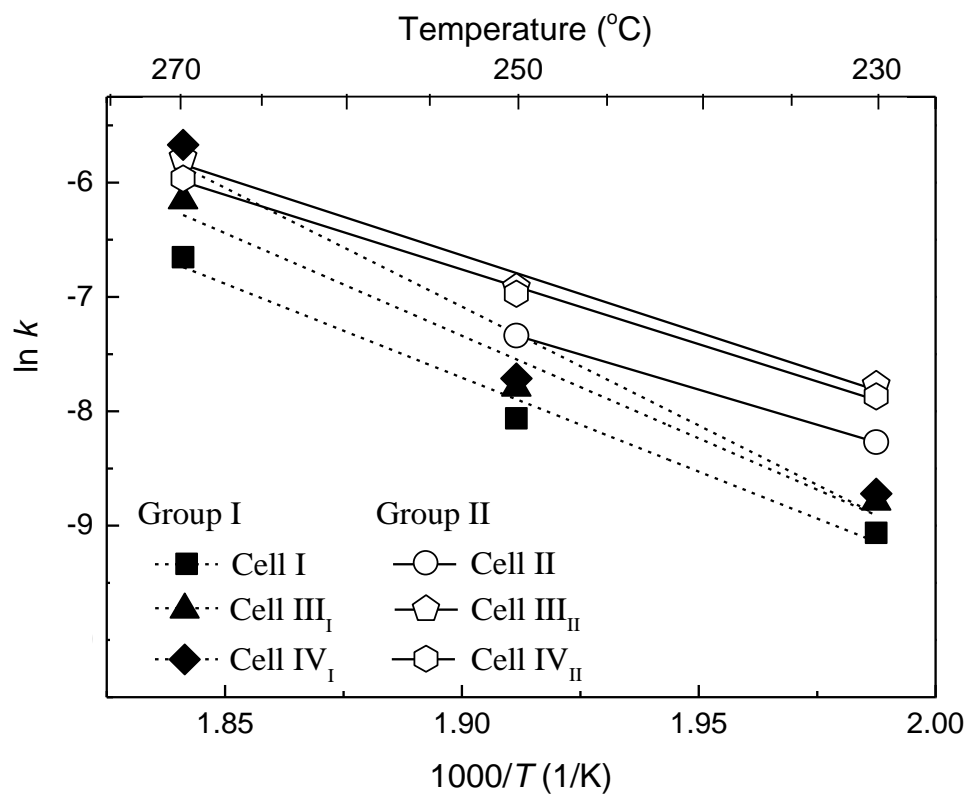


Fig. 2 The Arrhenius plot for various crystalline celluloses using pseudo-first order reaction kinetics as treated by semi-flow HCW at 230-270 $^{\circ}\text{C}$ /10 MPa/15 min

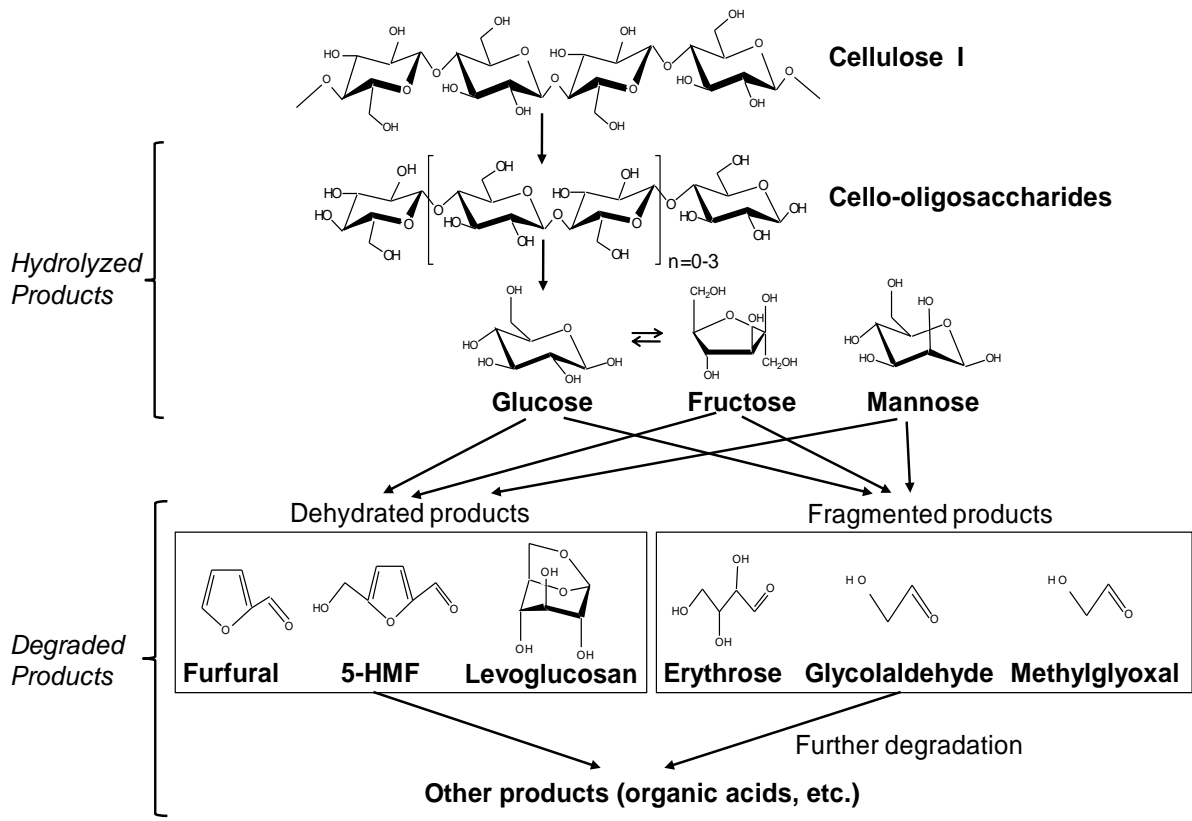


Fig. 3 Decomposition pathway of crystalline cellulose I as treated by semi-flow HCW

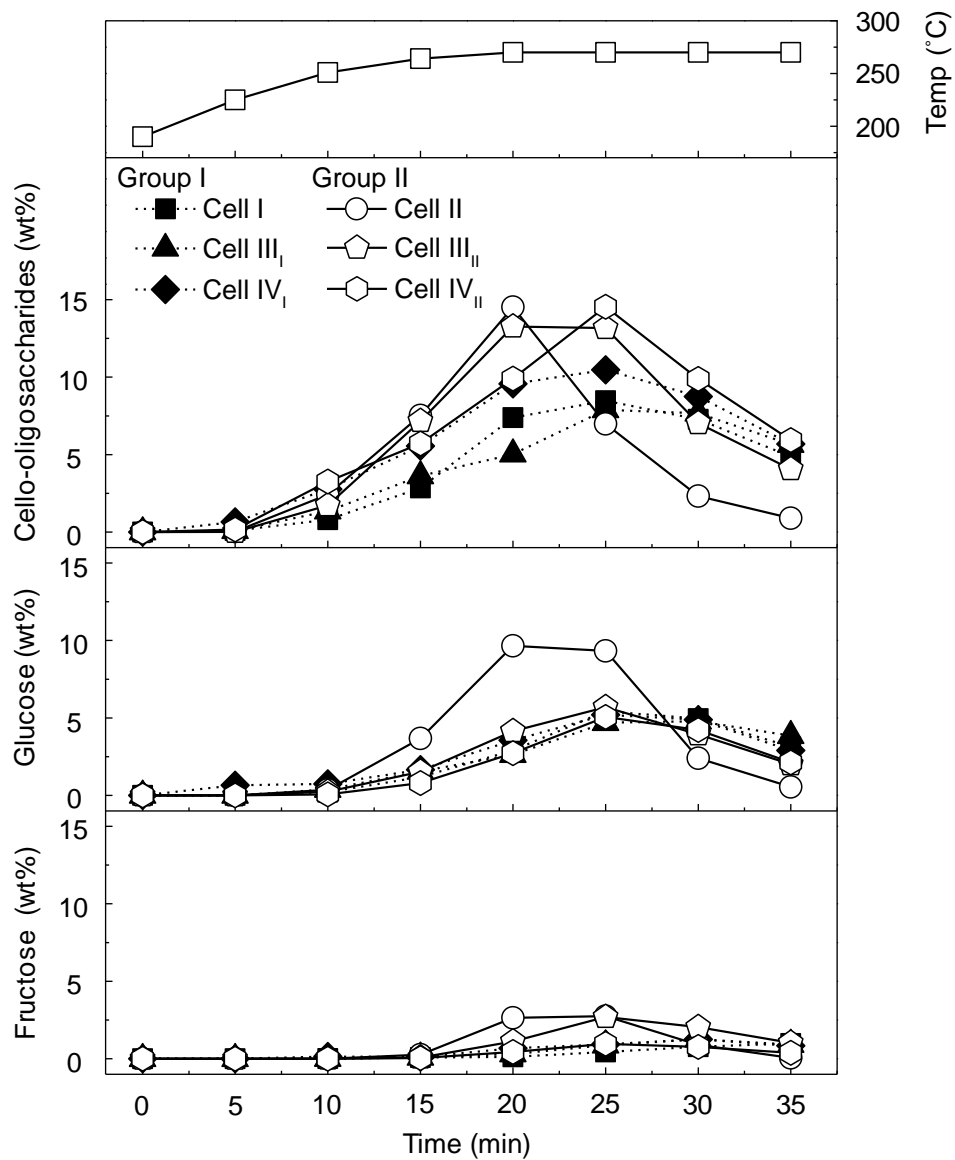


Fig. 4 The hydrolyzed products of cello-oligosaccharides, glucose and fructose in the WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min. Top figure corresponds to treatment temperature (*open squares*)

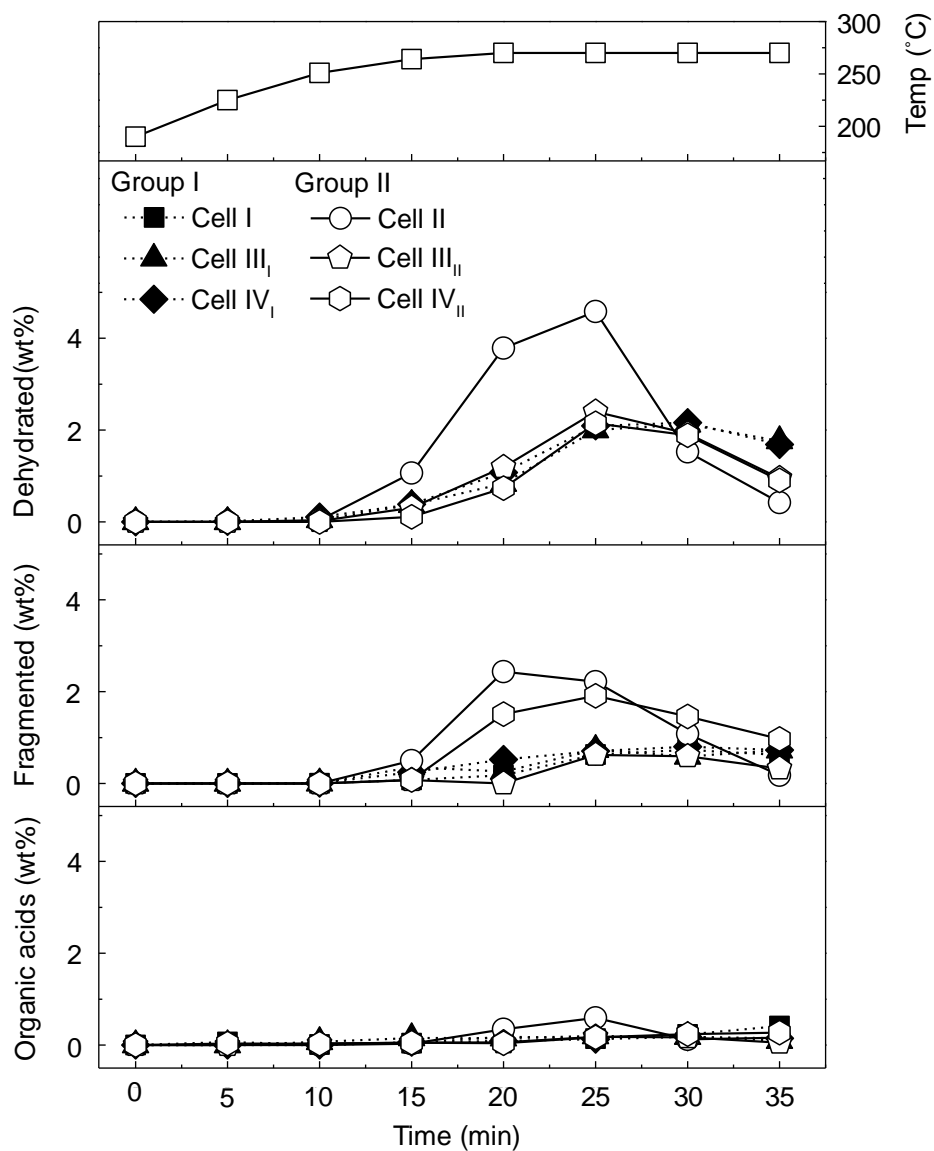


Fig. 5 The degraded products of dehydrated, fragmented and organic acids products in the WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min. Top figure corresponds to treatment temperature (*open squares*)

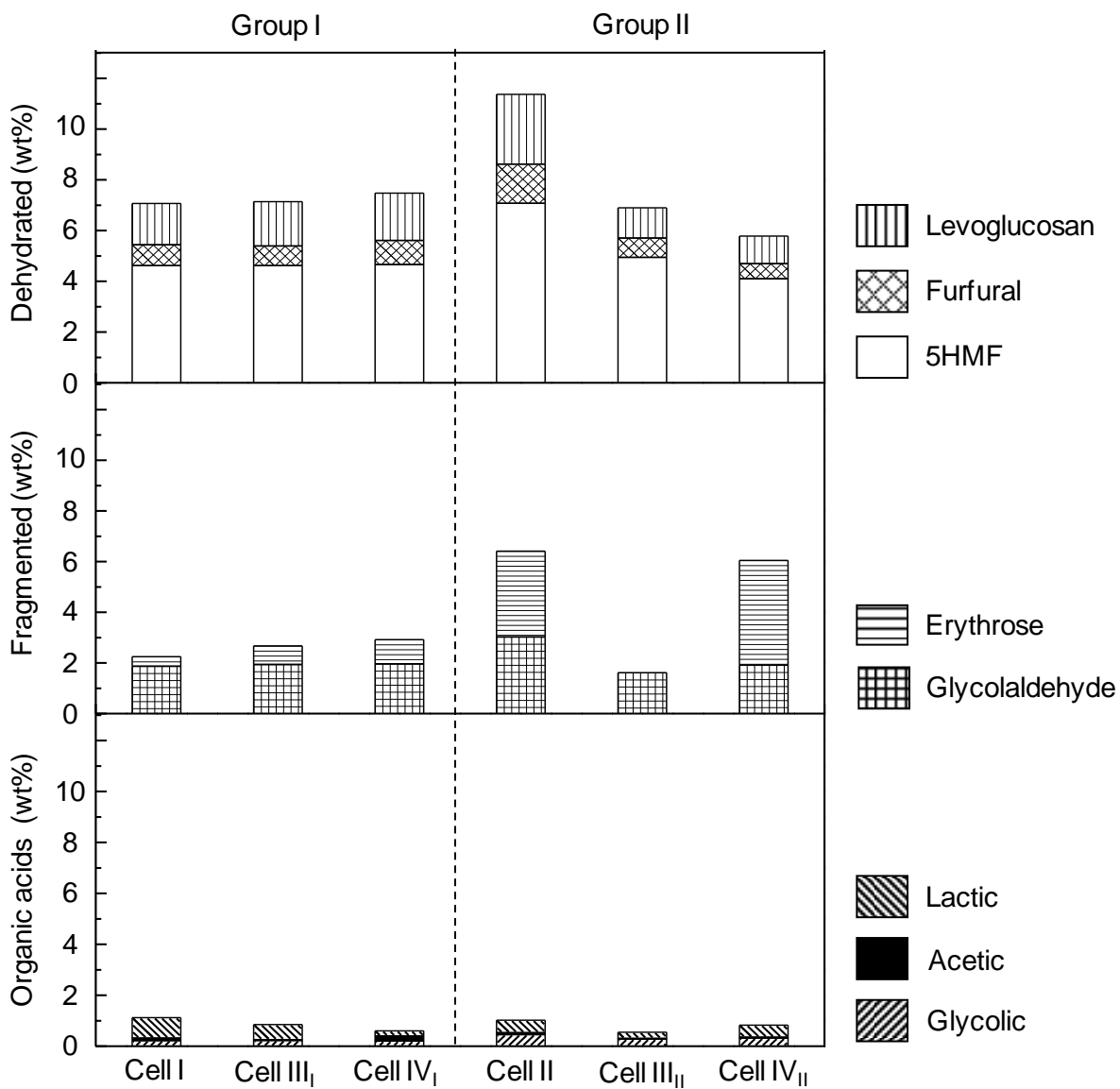


Fig. 6 The degraded products in WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min

Table 1 The crystallinity and *DP* for various types of crystalline celluloses prepared in this study

	Cellulose	Crystallinity (%)	<i>DP</i>
Group I	Cell I	92	176
	Cell III <sub>I</sub>	86	164
	Cell IV <sub>I</sub>	90	167
Group II	Cell II	85	173
	Cell III <sub>II</sub>	87	176
	Cell IV <sub>II</sub>	85	164



Table 2 The apparent activation energies of various types of crystalline celluloses as treated by semi-flow HCW at 230-270°C/10 MPa/15 min

	Cellulose	Activation energy, $E_a$ (kJ/mol)
Group I	Cell I	71.4
	Cell III <sub>I</sub>	78.0
	Cell IV <sub>I</sub>	90.2
Group II	Cell II	53.3
	Cell III <sub>II</sub>	59.0
	Cell IV <sub>II</sub>	56.6

Table 3 The total hydrolyzed and degraded products of WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min

	Cellulose	Hydrolyzed product (wt%)	Degraded product (wt%)
Group I	Cell I	52.0	10.5
	Cell III <sub>I</sub>	52.7	10.6
	Cell IV <sub>I</sub>	67.0	11.1
Group II	Cell II	67.3	18.8
	Cell III <sub>II</sub>	71.0	8.9
	Cell IV <sub>II</sub>	67.0	12.6